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The Mineral Nature of Asbestos

Malcolm Ross^{a,*}, Arthur M. Langer^b, Gordon L. Nord^c, Robert P. Nolan^d, Richard J. Lee^e,
D. Van Orden^f, John Addison^g

^{a,b,c,d}*Earth and Environmental Sciences of the Graduate School and University Center of The City
University of New York, 365 Fifth Avenue, New York, New York 10016, USA*

^{e,f}*R.J. Lee Group, Monroeville, PA, USA*

^g*John Addison Consultancy, Ltd, Cottingham, United Kingdom*

* Corresponding author. Phone: +1 202 338 6572
E-mail address: mrdrr@earthlink.net (Malcolm Ross)

Abstract

Fibrous minerals are common in nature but asbestiform minerals are rare. The unique mineralogical characteristic common to all the asbestos minerals is their morphologic form (or habit of crystallization) as polyfilamentous fiber bundles. The individual fibrils within the bundles have a tendency to be very long with a narrow range of diameters and grow with their long fiber axis in parallel orientation to the bundle length. The asbestiform habit imparts to the asbestos minerals sufficient flexibility and tensile strength so that most can be woven into cloth. In the past application has focused on their ability to insulate against the transfer of heat. However, these minerals possess other properties which make them useful in many industrial applications.

Keywords: Asbestos; Asbestiform; Fibrous

The ancient world made use of the asbestos minerals, invented the names amiantos and asbestos, and developed practical uses for these minerals which continue to the present. The enormous demand for asbestos, currently around 2,000,000 tons per year worldwide, developed over the last 120 years. The asbestiform minerals rarely occur in sufficient abundance to be of commercial importance; only one asbestiform serpentine mineral and five asbestiform amphibole minerals occur in such abundance. These six industrial minerals, known collectively as asbestos, share a unique set of physicochemical properties, although each can be distinguished from another by their chemical compositions and structure. The one serpentine asbestos mineral, chrysotile, crystallizes in the form of rolled up sheets structurally unique in nature and different from the double-chain structure that characterize the five amphibole minerals. The amphibole minerals can occur in habits which are not polyfilamentous and therefore are not classified as asbestos. These non-asbestos amphiboles occur commonly and represent 5% of the earth's crust.

The various words used in antiquity to denote the asbestos minerals, including asbestos, asbestus, asbestinon, asbest, asbeste, asbeston, abeston, amiantos, amiantus, amianthus, amiant, and amiante, can be traced back to the writings of the ancient Greek philosophers and their use of

two words— $\alpha\mu\iota\alpha\nu\tau\omicron\varsigma$ (amiantos) and $\alpha\sigma\beta\epsilon\sigma\tau\omicron\varsigma$ (asbestos). The Greek physician, Pedanius Dioscorides of Cilicia (40-90 A.D.) describes an "undefiled stone", $\alpha\mu\iota\alpha\nu\tau\omicron\varsigma$ $\lambda\iota\theta\omicron\varsigma$ —transliterated as amiantos lithos, which occurs in Cyprus. In modern Greek usage, the noun $\lambda\iota\theta\omicron\varsigma$ (lithos) is omitted and replaced with $\alpha\mu\iota\alpha\nu\tau\omicron\varsigma$ (amiantos). Dioscorides and other ancient Greek writers used the noun $\alpha\sigma\beta\epsilon\sigma\tau\omicron\varsigma$ (asbestos) to mean quicklime; a meaning retained in Modern Greek. However, Pliny the Elder apparently misunderstanding the use of this word by the early Greeks and replaced the Greek noun for quicklime, asbestos, with the Latin word asbestinon, or "asbestos." The familiar claim that the Romans knew the hazards of asbestos has its likely origin in mistranslating asbestos for quicklime, which was used on occasion by the Romans in battle to choke the enemy (Browne and Murray, 1990).

The ancient word took on a new meaning with the development of the science of mineralogy and the commercial use of the asbestos in the 19th Century. The term was used to describe a group of six minerals in commerce having the following desirable industrial properties:

- Long fibrous shape
- High tensile strength and flexibility
- Low thermal and electrical conductivity
- High absorbency
- High mechanical thermal stability
- Resistance to acids and bases.

Fibrous crystals of minerals are fairly common in nature but the formation of asbestiform minerals is rare; generally, minerals crystallize in more isometric shapes. The term fibrous includes other terms such as filiform, acicular, capillary, byssolitic and asbestiform. Asbestiform fibers are a particularly rare form of fibrous mineral. The unique mineralogical characteristic common to all of the asbestos minerals is that their morphologic form or habit of crystallization as polyfilamentous fiber bundles (see Fig. 1). The one serpentine and five amphibole minerals, which form the various types of commercial asbestos, more commonly, crystallize into other habits. The non-asbestos habits do not possess the desirable industrial properties noted above (see Fig. 2) (Langer et al., 1979; Ross et al., 1984). Asbestos forms in dilated rock either perpendicular (cross-fiber) or parallel (slip-fiber) to the opening in the rock (see Fig. 3). Slip fiber commonly forms along the compressed limbs of tight fold in the host rock. Minerals other than the commercial asbestos minerals can, albeit rarely, crystallize in the asbestiform habit. While the clay mineral palygorskite occurs naturally, it almost exclusively forms with an asbestiform habit (Zoltai 1981; Nolan et al., 1991). For example, other amphibole minerals, potassium winchite and richterite occur occasionally in asbestiform habit (Wylie and Higgins, 1980; Verkouteren and Wylie, 2000). Another amphibole, asbestiform fluoro-edenite has been described from Biancavilla in Sicily (Gianfagna and Oberti, 2001; Gianfagna et al., 2003).

Although the amphibole mineral group accounts for approximately 5% by volume of the earth's crustal mineralogy (Liebau, 1985), deposits of asbestos large enough to be commercially viable are rare. Small quantities of asbestos have been used since ancient times. With the needs of industry in the last decades of the 19th Century, exploitation became important; the fibers have physicochemical properties that made them useful in many applications (Alleman and Mossman, 1997). Since that time, more than 95% of the commercially developed asbestos ore deposits

were of chrysotile asbestos, the geologically most abundant type of asbestos (Ross and Virta, 2001). Currently, chrysotile asbestos is mined in Russia, China, Kazakhstan, Canada and Brazil. The remaining percentage was amphibole asbestos, predominately crocidolite and amosite. Although anthophyllite asbestos and tremolite asbestos have been mined to minor extents, a Finnish anthophyllite asbestos mine at Paakkila operated from 1918 to 1977. Anthophyllite and tremolite have been extensively mined from a number of small deposits across the state of Rajasthan in India (Mansinghka and Ranawat, 1996). Only these six commercial minerals are considered asbestos and are regulated under the various asbestos exposure standards (see Table 1).

With a few exceptions, commercially viable asbestos deposits contain 2-4% asbestos in the ore body. All of the major commercial asbestos fiber types have been mined in the Republic of South Africa although mines operate there today. Crocidolite mining also occurred in Australia and Bolivia. Current worldwide mining of amphibole asbestos, if it occurs, is on a very limited basis while current worldwide chrysotile asbestos production is approximately 2×10^6 tons per year.

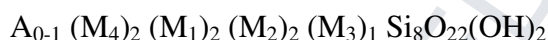
The mention of asbestos in the ancient world most likely referred to chrysotile asbestos and tremolite asbestos (Browne and Murray, 1990; Ross and Nolan, 2003). Prior to the modern scientific age, knowledge of the differences between the various asbestos fiber types would not have been understood in a meaningful way. Interest focused on the remarkable properties of the mineral, the flexibility and tensile strength which allowed it to be spun into cloth. The high temperature stability allowing novel applications such as cremation wrappings made by the Romans to collect the ashes of the Emperors, external wicks for the lamps of the Vestal Virgins and the legendary tablecloth of Charlemagne reportedly cleaned by being placed in the fire after dinner for the amusement of his guests.

Knowledge concerning the elemental compositions and crystal structure of amphibole and serpentine minerals developed in the 19th and 20th Century respectively. It was known to 19th Century mineralogists that minerals crystallizing in the asbestiform habit had higher tensile strength and flexibility than those crystallizing in the more common acicular or prismatic form (Zoltia, 1978; Langer et al., 1979). By the time of World War I, the elemental composition of many amphiboles had been determined and analysis of the morphology of large single crystals indicated the amphibole crystal class was either monoclinic or orthorhombic. By 1916, the chemical formula of tremolite, one of the simplest and most common of the amphibole group minerals, was well known to be $[\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2]$ and belonged to the monoclinic crystal class. With the development of x-ray diffraction methods it was becoming possible to determine the arrangements of the atoms in the cell and therefore the number of chemical formula in the unit. Warren, (1929) reported the first crystal structure of an amphibole – tremolite. The similarity of the amphibole structure allowed Warren (1930) to report on four more monoclinic amphiboles – kupferite, actinolite, hornblende and grunerite. Further research would show that the various amphiboles with the monoclinic structure type would most commonly have C2/m space group symmetry (Hawthorne, 1983). Also, Warren (1930) would report the crystal structure of anthophyllite to be orthorhombic. All naturally occurring orthorhombic amphiboles so far identified belong to the space group Pnma (Hawthorne, 1983). The polyfilamentous bundles elongate along the c-axis with the fibrils parallel. The unit fibrils are disorientated in the ab-plane; asbestiform monoclinic amphiboles have parallel extinction in polarized light rather than the inclined extinction expected for monoclinic amphiboles (see Fig. 4) (Wylie, 1979; Dorling and Zussman, 1986; Langer et al., 1991).

The essential structural features of the amphibole group are the following:

- Silica tetrahedral groups form a double chain with the repeating single chain unit having the composition $\text{Si}_4\text{O}_{11}^{6-}$ (see Fig. 1). All amphiboles are characterized by double chains of linked silica tetrahedral that repeat every 5.3\AA and lie parallel to the c-axis, almost always the direction of elongation in amphiboles. There are 8 silicon atoms in the tetrahedral site per chemical formula unit. Aluminum can substitute for silicon in up to two of 8 tetrahedral. Aluminum is not normally found in the commercial asbestos amphiboles but can be found in richterite, edenite and winchite.
- The silica chain structure is four octahedra wide. These octahedral sites form four crystallographically distinct cation sites referred to as M_1 , M_2 , M_3 and M_4 . These four types of octahedral sites contain the seven cations per formula unit: two in the M_1 sites, two in the M_2 sites, one in the M_3 site and two in the M_4 sites. Two octahedral corners in each chemical formula are not shared with the silica tetrahedral; generally these corners are occupied by hydroxyl groups.
- Between the double chains, within the 6-fold rings of linked silica tetrahedral, there is an additional row of sites referred to as the A sites. These can be occupied by large cations (e.g., sodium or potassium only). These sites are never fully occupied in amphibole minerals, and rarely occupied in the asbestiform amphiboles.

The M_1 , M_2 and M_3 octahedral sites form a chain consisting of five cations per chemical formula, which are between the opposite facing six-fold rings of silica tetrahedral. The octahedral chains are linked by the large M_4 cations. Additional large ions can be found in the A structural site. The general formula for all amphibole composition is:



A = Na⁺ or K⁺ in 10- or 12-fold coordination

M_4 = Ca²⁺, Na⁺, Mn²⁺, Fe²⁺ and Mg²⁺ in six or eight fold coordination

M_1 , M_2 and M_3 = Mg²⁺, Fe²⁺, Mn²⁺, Fe³⁺ in 6-fold coordination. Si⁴⁺ in the tetrahedral sites forms the double chains.

Complete substitutions can occur between Na⁺ and Ca⁺ and between Mg²⁺ and Fe²⁺ or Mn²⁺.

These dissimilar octahedral sites can accommodate seven atoms of different sizes and valences allowing the amphibole group to have complex and far ranging element compositions. The amphibole group of minerals is made up of 27 separate mineral types with a large number of varietal species based on 23 chemical species (Whittaker, 1979; Veblen and Wylie 1993 Leake, 1997). Those crystallizing in the asbestiform habit have the designation "asbestos" added after the mineral name.

Chrysotile asbestos is a serpentine mineral, the crystal structure of which is formed by a double layer composed of a tetrahedral and octahedral sheet: the tetrahedral and octahedral sheets having the composition $[n \text{ Si}_2\text{O}_5]_{2n}$ and the other a nonsilicate sheet of $[\text{Mg}_3\text{O}_2(\text{OH})_4]n^{2n+}$, respectively. The two other common serpentine minerals are lizardite and antigorite. Chrysotile asbestos is the only member of the serpentine group of any importance as a commercial mineral. It is the sixth mineral regulated under the asbestos standards and currently the only asbestos mineral of commercial importance with worldwide production of 2 million metric tons in 2001 (Virta, 2003).

The basic units of the tetrahedral sheets are six-membered rings, having pseudohexagonal or trigonal symmetry. These rings are similar to those found in the amphibole double chains. The amphibole chains differ in that the growth is restricted to a single direction to form chains, whereas in chrysotile asbestos growth extends in two directions to follow an effectively infinite sheet. The octahedral sheet is formed by magnesium octahedrally coordinated with oxygen and hydroxyl groups and is similar to that found in brucite. The dimensions of the two sheets differ. Attention is generally focused on the b axis of the octahedral sheet, which is larger than the same axial direction in the tetrahedral sheet (9.45Å compared with 9.15Å). The dimensional mismatch of the octahedral and tetrahedral sheets can cause the double sheets to roll up into cylindrical tubes with the layer octahedral portion of the double layer forming to exterior of the curved surface. These fibrils are the ultimate minimum diameter that can be found in chrysotile and generally have a diameter around 25 nanometers. Usually, polygonal forms of chrysotile also occur rarely. The outer octahedral layer of chrysotile is readily leached of magnesium, even under mildly acid conditions (Hume and Rimstidt, 1992), and indeed chrysotile is now known to have a lower chemical durability than the amphibole asbestos minerals for this reason.

References

- Alleman, J.E., Mossman, B.T., 1997. Asbestos Revisited. *Sci Amer* July, 70-75.
- Browne, K., Murray, R., 1990. Asbestos and the Romans. *The Lancet* 336,445.
- Dorling, M., Zussman, J., 1986. Characteristics of Asbestiform and Non-Asbestiform Amphiboles. *Lithos* 20, 469-489.
- Gianfagna, A., Oberti, R., 2001. Fluoro-edenite from Biancavilla (Catania, Sicily, Italy): Crystal chemistry of a new amphibole end-member. *Amer Miner* 86, 1489-1493.
- Gianfagna, A., Ballirano, P., Bellatreccia, F., Bruni, B., Paoletti, L., Oberti, R., 2003. Characterization of amphibole asbestos linked to mesothelioma in the area of Biancavilla, Eastern Sicily, Italy. *Min Mag* 67, 1221-1229.
- Hawthorne, F.C., 1983. The Crystal Chemistry of the Amphiboles. *The Canadian Mineralogist*, 21, 173-480.
- Hume, L.A., Rimstidt, J.D., 1992. The biodurability of chrysotile asbestos. *Am Miner* 77, 1112-1128.

- Langer, A.M., Rohl, A.N., Wolff, M.S., Selikoff, I.J., 1979. Asbestos, fibrous minerals and acicular cleavage fragments: nomenclature and biological properties, in: Dement, J.M., Lemen, R.A. (Eds.), *Dust and Disease Society for Occupational and Environmental Health*. Pathox Publishers, Illinois, pp. 1-22.
- Langer, A.M., Nolan, R.P., Addison, J., 1991. Distinguishing between amphibole asbestos Fibers and elongate cleavage fragments of their non-asbestos analogues, in: Brown, R.C., Hoskins, J.A., Johnson, N.F. (Eds.), *Mechanisms of Fiber Carcinogenesis*. NATO ASI Series, Plenum Press, New York and London, pp. 253-267.
- Leake, B.E. et al., 1997. Nomenclature of Amphiboles: Report of the Subcommittee on Amphiboles of the International Mineralogical Association. Committee on New Minerals and Mineral Names. *Can Mineral* 35, 219-246.
- Liebau, F., 1985. *Structural Chemistry of Silicates*, Springer-Verlag, Berlin.
- Nolan, R.P., Langer, A.M., Herson, G.B., 1991. Characterization of Paolygarskite Specimens from Different Geological Locales for Health Hazard Evaluation. *Br J Indust Med* 48, 463-475.
- Ross, M., Nolan, R.P., 2003. History of asbestos discovery and use and asbestos-related disease in context with the occurrence of asbestos with ophiolite complexes, in: Dilek, Y., Newcomb, S., (Eds.), *Ophiolite Concept and the Evolution of Geological Thought*. Geological Society of America, Special Paper 373, pp. 447-470.
- Ross, M., Kuntze, R.A., Clifton, R.A., 1984. A Definition for Asbestos. Special Technical Publication 834. American Society for Testing Materials, Philadelphia, pp. 139-147.
- Ross, M., Virta, R.L., 2001. Occurrence, production and uses of asbestos, in: Nolan, R.P., Langer, A.M., Ross, M., Wicks, F.J., Martin, R.F. (Eds.), *The Health Effects of Chrysotile Asbestos*. The Canadian Mineralogist, Special Publication 5, Ottawa, pp. 79-88.
- Veblen, D.R., Wylie, A.G., 1993. Mineralogy of Amphiboles and 1:1 Layer Silicates, in: Guthrie, G.D., Mossman, B.T. (Eds.), *Health Effects of Mineral Dust Reviews*. Mineralogy, 28, Washington DC, pp. 61-137.
- Verkouteren, J.R., Wylie, A.G., 2000. The tremolite-ferro-actinolite series: systematic relationships among cell parameters, composition, optical properties, and habit, and evidence of discontinuities. *Amer Min* 85, 1239-1254.
(<http://minerals.usgs.gov/minerals/pubs/commodity/asbestos/>). Accessed March 23, 2004).
- Warren, B.E., 1929. The structure of tremolite $\text{H}_2\text{Ca}_2\text{Mg}_5(\text{SiO}_3)_8$. *Z Krist* 72, 42-57.
- Warren, B.E., 1930. The crystal structure and chemical composition of the monoclinic amphiboles. *Z Krist* 75, 161-178.

- Warren, B.E., Modell, D.I., 1930. The structure of anthophyllite $\text{H}_2\text{Ca}_2\text{Mg}_5(\text{SiO}_3)_8$. *Z Krist* 75, 161-178.
- Whittaker, E.J.W., 1979. Mineralogy, chemistry and crystallography of amphibole asbestos, in: Ledoux, R.L. (Ed.), *Short Course in Mineralogical Techniques of Asbestos Determination*. Mineralogical Association of Canada, Ottawa, pp. 1-34.
- Wylie, A.G., 1979. Optical properties of fibrous amphibole, in: Selikoff, I.J., Hammond, E.C. (Eds.), *Health Hazards of Asbestos Exposure*. Annals of the NY Academy of Sciences, New York, pp. 611-619.
- Wylie, A.G., Huggins, C.W., 1980. Characteristics of potassium winchite asbestos from the Allamore Talc District, Texas. *Canadian Min* 18, 101-107.
- Wylie, A.G., Verkouteren, J.R., 2000. Amphibole asbestos from Libby, Montana: aspects of nomenclature. *Amer Min* 85, 1540-1542.
- Zoltai, T., 1978. History of asbestos-related mineralogical terminology, in: Gravatt, C.C., LaFleur, P.D., Heinrick, K.F.J. (Eds.), *Workshop on Asbestos: Definitions and Measurement Methods*. National Bureau of Standards, Special Publication 506, Maryland, pp. 1-18.
- Zoltai, T., 1981. Amphibole asbestos mineralogy, in: Veblen, D.R. (Ed.), *Amphiboles and Other Hydrous Pyriboles-Mineralogy*. Mineralogical Society of America, Washington, DC, pp. 237-278.